Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic 3d\textsuperscript{1} Perovskites

E. Pavarini,\textsuperscript{1} S. Biermann,\textsuperscript{2} A. Poteryaev,\textsuperscript{3} A. I. Lichtenstein,\textsuperscript{3} A. Georges,\textsuperscript{2} and O. K. Andersen\textsuperscript{4}

\textsuperscript{1}INFM and Dipartimento di Fisica "A. Volta," Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy
\textsuperscript{2}Centre de Physique Théorique, Ecole Polytechnique, 91128 Palaiseau Cedex, France
\textsuperscript{3}NSRF\textsuperscript{M}, University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands
\textsuperscript{4}Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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Using $t_{2g}$ Wannier functions, a low-energy Hamiltonian is derived for orthorhombic 3d\textsuperscript{1} transition-metal oxides. Electronic correlations are treated with a new implementation of dynamical mean-field theory for noncubic systems. Good agreement with photoemission data is obtained. The interplay of correlation effects and cation covalency (GdFeO\textsubscript{3}-type distortions) is found to suppress orbital fluctuations in LaTiO\textsubscript{3} and even more in YTiO\textsubscript{3}, and to favor the transition to the insulating state.

Transition-metal perovskites have attracted much interest because of their unusual electronic and magnetic properties arising from narrow 3d bands and strong Coulomb correlations \cite{1}. The 3d\textsuperscript{1} perovskites are particularly interesting, since seemingly similar materials have very different electronic properties: SrVO\textsubscript{3} and CaVO\textsubscript{3} are correlated metals with mass enhancements of, respectively, 2.7 and 3.6 \cite{2}, while LaTiO\textsubscript{3} and YTiO\textsubscript{3} are Mott insulators with gaps of, respectively, 0.2 and 1 eV \cite{3}.

In the Mott-Hubbard picture the metal-insulator transition occurs when the ratio of the on-site Coulomb repulsion to the one-electron bandwidth exceeds a critical value $U_c/W$, which increases with orbital degeneracy \cite{4,5}. In the ABO\textsubscript{3} perovskites the transition-metal ions (B) are on a nearly cubic (orthorhombic) lattice and at the centers of corner-sharing O\textsubscript{6} octahedra. The 3d band splits into $pd\pi$-coupled $t_{2g}$ bands and $p\sigma\pi$-coupled $e_g$ bands, of which the former lie lower, have less O character and couple less to the octahedra than the latter. The simplest theories for the $d^1$ perovskites \cite{1} are therefore based on a Hubbard model with three degenerate $e_g$-filled $t_{2g}$ bands per B ion, and the variation of the electronic properties along the series is ascribed to a progressive reduction of $W$ due to the increased bending of the $pd\pi$ hopping paths (BOB bonds).

This may not be the full explanation of the Mott transition however, because a splitting of the $t_{2g}$ levels can effectively lower the degeneracy. In the correlated metal, the relevant energy scale is the reduced bandwidth associated with quasiparticle excitations. Close to the transition, this scale is of order $\sim ZW$, with $Z \approx 1 - U/U_c$, and hence much smaller than the original bandwidth $W$. A level splitting by merely $ZW$ is sufficient to lower the effective degeneracy all the way from a threefold to a nondegenerate single band \cite{6}. This makes the insulating state more favorable by reducing $U_c/W$ \cite{5,6}. Unlike the $e_g$-band perovskites, such as LaMnO\textsubscript{3}, where large (10\%) cooperative Jahn-Teller (JT) distortions of the octahedra indicate that the orbitals are spatially ordered, in the $t_{2g}$-band perovskites the octahedra are almost perfect. The $t_{2g}$ orbitals have therefore often been assumed to be degenerate. If that is true, it is conceivable that quantum fluctuations lead to an orbital liquid \cite{7} rather than orbital ordering. An important experimental constraint on the nature of the orbital physics is the observation of an isotropic, small-gap spin-wave spectrum in both insulators \cite{8}. This is remarkable because LaTiO\textsubscript{3} is a $G$-type antiferromagnet with $T_N = 140$ K, $m = 0.45\mu_B$, and a 3\% JT stretching along a \cite{9}, while YTiO\textsubscript{3} is a ferromagnet with $T_c = 30$ K, $m_0 = 0.8\mu_B$, and a 3\% stretching along y on sites 1 and 3, and x on 2 and 4 \cite{10} (see Fig. 1).

FIG. 1 (color). $Pbnm$ primitive cells (right panels), subcells 1 (left panels), and the occupied $t_{2g}$ orbitals for LaTiO\textsubscript{3} (top panels) and YTiO\textsubscript{3} (bottom panels) according to the LDA + DMFT calculation. The oxygens are violet, the octahedra yellow, and the cations orange. In the global, cubic $xyz$ system directed approximately along the Ti-O bonds, the orthorhombic translations are $a = (1, -1, 0)(1 + \alpha)$, $b = (1, 1, 0)(1 + \beta)$, and $c = (0, 0, 2)(1 + \gamma)$, with $\alpha$, $\beta$, and $\gamma$ small. The Ti sites 1 to 4 are a/2, b/2, (a + c)/2, and (b + c)/2. The La(Y) ab plane is a mirror $(z \leftrightarrow -z)$ and so is the Ti hc plane $(x \leftrightarrow y)$ when combined with the translation $(b - a)/2$. 

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We shall find that the $t_{2g}$ degeneracy is lifted at the classical level. This is not due to the small JT distortions via $O_B$ $pd\pi$ coupling, but to the GdFeO$_3$-type distortion which tilts the corner-sharing octahedra around the $b$ axis (by $0^\circ$, $9^\circ$, $12^\circ$, and $20^\circ$) and rotates them around the $c$ axis (by $0^\circ$, $7^\circ$, $9^\circ$, and $13^\circ$), as we progress from cubic SrVO$_3$ via CaVO$_3$ and LaTiO$_3$ to YTiO$_3$ [9–12]. This distortion is driven by the increasing oxygen-cation (OA) $pd\sigma$ covalency, and it primarily pulls closer four of the 12 oxygens neighboring a given cation [13]. Moreover, two to four of the eight cations neighboring a given B ion are pulled closer [14]. The $t_{2g}$ orbitals couple to the OA distortion via oxygen (BOA $dp\pi$-$pd\sigma$), and they couple directly (AB $dd\sigma$) to the AB distortion. As seen in Fig. 1, the orthorhombic GdFeO$_3$-type distortion also leads to quadrupling of the cell. These findings are consistent with conclusions drawn in the most recent model Hartree-Fock study [15]. The correct magnetic orders in LaTiO$_3$ and YTiO$_3$ were also obtained with the LDA $+ U$ method [16]. The predicted moment and orbital order in YTiO$_3$ were confirmed by NMR [17] and neutron scattering [18], but not in LaTiO$_3$. These static mean-field methods are not appropriate for the metallic systems, however.

In this Letter, we shall (i) present a new implementation of a many-body method [19,20], which allows for a quantitative, material-specific description of both the Mott transition and the orbital physics, and (ii) use it to explain why some of the $d^1$ perovskites are metallic and others are insulators, why the metals have different mass enhancements and the insulators different gaps. Such properties can be described by a low-energy, multiband Hubbard Hamiltonian,

$$H = H^{\text{LDA}} + \frac{1}{2} \sum_{imm'\sigma} U_{mmn} n_{imm} n_{imm'} - \sigma + \frac{1}{2} \sum_{im(m'\sigma)} (U_{mm'} - J_{mm'}) n_{imm} n_{imm'} \sigma,$$

where $n_{imm} =$ $a^+_{im\sigma} a_{im\sigma}$, and $a^+_{im\sigma}$ creates an electron with spin $\sigma$ in a localized orbital $m$ at site $i$. This Hamiltonian depends on how the $imm$ orbitals are chosen. $H^{\text{LDA}}$ is the one-electron part given by density-functional theory [LDA (local-density approximation)], which should provide the proper material dependence. Recently it has become feasible to solve (1) using the dynamical mean-field theory (DMFT) [19] and to obtain realistic physical properties [20]. In the original LDA $+ DMFT$ implementations it was assumed that the on-site block(s) of the single-particle Green function is diagonal in the space of the correlated orbitals, and these were taken as orthonormal linear muffin-tin orbitals (LMTOs) approximated by truncated and renormalized partial waves.

Although these approximations are good for cubic $t_{2g}$ systems such as SrVO$_3$ [21], they deteriorate with the degree of distortion. Our new implementation of LDA $+ DMFT$ uses a set of localized Wannier functions in order to construct a realistic Hamiltonian (1), which is then solved by DMFT, including the nondiagonal part of the on-site self-energy.

For an isolated set of bands, a set of Wannier functions constitutes a complete, orthonormal set of orbitals with one orbital per band. For the $d^1$ perovskites we take the correlated orbitals to be three localized $t_{2g}$ Wannier orbitals, and in $H^{\text{LDA}}$ we neglect the degrees of freedom from all other bands. In order to be complete, such a Wannier orbital must have a tail with, e.g., $O$ $p\pi$ and $A$ $d$ characters. Our Wannier orbitals are symmetrically orthonormalized $N$th-order muffin-tin orbitals (NMTOs) [22], which have all partial waves other than B $xy$, $yz$, and $zx$ downfolded. Such a $t_{2g}$ NMTO can have on-site $e_g$ character and that allows the orbital to orient itself after the surroundings, although $xy$, $yz$, and $zx$ refers to the global cubic axes defined in Fig. 1. Fourier transformation of the orthonormalized $12 \times 12$ NMTO Hamiltonian, $H^{\text{LDA}}(k)$, yields on-site blocks and hopping integrals. For the on-site Coulomb interactions in Eq. (1), we use the common assumption that, as in the isotropic case, they can be expressed in terms of two parameters: $U_{mm'} = U$, $U_{mm'} = U - 2J$, and $J_{mm'(\sigma\sigma')} = J$ [23]. From Ref. [24], $J = 0.68$ eV for the vanadates and 0.64 eV for the titanates. Since our Hamiltonian involves only correlated orbitals, so that the number of correlated electrons is fixed, the double-counting correction amounts to an irrelevant shift of the chemical potential. $H$ is now solved within DMFT, i.e., under the assumption that the components of the self-energy between different sites can be neglected. As a result, the self-energy can be obtained from the solution of an effective local impurity model which involves only three correlated orbitals. In contrast to all previous studies, we take all components of the self-energy matrix $S_{mm'}$ between different Wannier functions on a given B site into account [25]. From this $3 \times 3$ matrix, by use of the $Pbnm$ symmetry (Fig. 1), we construct a $12 \times 12$ block-diagonal self-energy matrix. The latter is then used together with $H^{\text{LDA}}(k)$ to obtain the Green function at a given $k$ point. Fourier transformation over the entire Brillouin zone yields the local Green function associated with a primitive cell, and its $3 \times 3$ on-site block is used in the DMFT self-consistency condition in the usual manner. The 3-orbital impurity problem is solved by a numerically exact quantum Monte Carlo (QMC) scheme [26]. To access temperatures down to 770 K, we use up to 100 slices in imaginary time. $10^6$ QMC sweeps and 15–20 DMFT iterations suffice to reach convergence. Finally, the spectral function is obtained using the maximum entropy method [27].

We now present the LDA results for the four perovskites. Figure 2 displays the on-site density of states (DOS) matrix $N_{mm}(\epsilon)$ in the representation of the $xy$, $yz$, and $zx$ Wannier functions. SrVO$_3$ is cubic and its $t_{2g}$ band with a width $W = 2.8$ eV consists of three non-interacting subbands, each of which is nearly 2D and gives rise to a nearly logarithmic DOS peak. In CaVO$_3$,
Going from the vanadates to the titanates, the effects of OA covalency, which drives this distortion. The energy of the \( xy \) Wannier orbital (the center of gravity of \( N_{xy,xy} \)) is 80 meV lower than that of the degenerate \( xz \) and \( yz \) orbitals, and small off-diagonal DOS elements appear. Going from the vanadates to the titanates, the effects of OA and (Ad) (Bt2g) covalency increase dramatically, because now A and B are 1st- rather than 3rd-nearest neighbors in the periodic table. As a consequence, the increased misalignment and loss of oxygen character reduce the bandwidths to 2.1 and 2.0 eV in LaTiO3 and YTiO3, and weak hybridization with the A \( d \) bands deforms the \( t_{2g} \) band. A pseudogap which starts out as a splitting of the \( t_{2g} \) band of the van Hove peak in CaVO3 deepens and moves to lower occupancy as we progress to LaTiO3 and YTiO3. The deep pseudogap in YTiO3 is mainly caused by the hybridization with the Y \( xy \) orbital. The \( xy \), \( yz \), and \( xz \) Wannier orbitals are now strongly mixed and diagonalized of the on-site blocks of \( H_{\text{LDA}} \) yields three singly degenerate levels with the middle (highest) being 140 (200) meV above the lowest in LaTiO3 and 200 (330) meV in YTiO3. This splitting is not only an order of magnitude smaller than the \( t_{2g} \) bandwidth, but also smaller than the subband widths, in particular, for LaTiO3. As a consequence, the eigenfunction for the lowest level is occupied by merely 0.45 electron in LaTiO3 and 0.50 in YTiO3, while the remaining 0.55 (0.50) electron occupies the two other eigenfunctions. The eigenfunction on site 1 with the lowest energy is \( 0.604|xy\rangle + 0.353|xz\rangle + 0.714|yz\rangle \) in LaTiO3 and \( 0.619|xy\rangle - 0.073|xz\rangle + 0.782|yz\rangle \) in YTiO3. The splittings are large compared with the spin-orbit splitting (20 meV) and \( kT \), and they are not caused by the JT distortions, as we have verified by turning them off in the calculations.

Next, we turn to the LDA + DMFT results. Calculations were performed for several values of \( U \) between 3 and 6 eV. We found that the critical ratio \( U_c/W \) decreases when going along the series: SrVO3, CaVO3, LaTiO3, and YTiO3. This is consistent with the increasing splitting of the \( t_{2g} \) levels and indicates that the Mott transition in the \( d^1 \) series is driven as much by the decrease of effective degeneracy as by the reduction of the bandwidth. The main features of the photoemission spectra for all four materials, as well as the correct values of the Mott-Hubbard gap for the insulators [3], are reproduced by taking \( U \) constant \( \sim 5 \) eV. This is satisfying because \( U \) is expected to be similar for vanadates and titanates, although slightly smaller for the latter [24]. In Fig. 3 we show the DMFT spectral functions together with the LDA total DOS. For cubic SrVO3 we reproduce the results of previous calculations [21,28]: the lower Hubbard band (LHB) is around \(-1.8 \) eV and the upper Hubbard band (UHB) around 3 eV. Going to CaVO3, the quasiparticle peak loses weight to the LHB which remains at \(-1.8 \) eV while the UHB moves down to 2.5 eV. These results are in good agreement with photoemission data [29] and show that SrVO3 and CaVO3 are rather similar, with the latter slightly more correlated. Similar conclusions were drawn in Ref. [21]. From the linear regime of the self-energy at small Matsubara frequencies we estimate the quasiparticle weight to be \( Z = 0.45 \) for SrVO3 and 0.29 for CaVO3. For a \( k \)-independent self-energy, as assumed in DMFT, this yields \( m^*/m = 1/Z = 2.2 \) for SrVO3 and 3.5 for CaVO3, in reasonable agreement with the optical conductivity values 2.7 and 3.6 [2].

For LaTiO3 and YTiO3 the LHB is around \(-1.5 \) eV, in accord with photoemission [30]. Despite very similar bandwidths, the gaps are very different, 0.3 and 1 eV, and this also agrees with experiments [3]. This is consistent with our findings that the \( t_{2g} \)-level splittings are smaller and \( U_c/W \) is larger in LaTiO3 than in YTiO3 where the orbital degeneracy is effectively 1. Diagonalization of the matrix of occupation numbers reveals that for the titanates one orbital per site is nearly full, in contrast to LDA. It contains 0.88 electron in LaTiO3 and 0.96 in YTiO3. The orbital polarization increases

![FIG. 2 (color). \( t_{2g} \) LDA DOS matrix (states/eV/spin/band) in the Wannier representation. On-site-1 elements: \( N_{yz,xz} \) (red), \( N_{xy,xy} \) (green), and \( N_{xy,yz} \) (blue). Insets: \( N_{yz,xz} \) (red), \( N_{xz,xy} \) (green), and \( N_{xy,yz} \) (blue). \( \epsilon_F = 0 \).](image1.png)

![FIG. 3. DMFT spectral function at \( T = 770 \) K (thick line) and LDA DOS (thin line). \( \mu = 0 \).](image2.png)
around the metal-insulator transition and becomes complete thereafter. Thus, for the vanadates, each orbital is approximately 1/3 occupied for all $U$ in the range 0 to 6 eV. The nearly complete orbital polarization found by LDA + DMFT for the two insulators indicates that correlation effects in the paramagnetic Mott insulating state considerably decrease orbital fluctuations and makes it unlikely that YTiO$_3$ is a realization of an orbital liquid [7]. In LaTiO$_3$ some orbital fluctuations are still active, although quite weak. The occupied orbital in LDA + DMFT is 0.586$|xy\rangle + 0.275|xz\rangle + 0.762|yz\rangle$ for LaTiO$_3$ and 0.622$|xy\rangle - 0.029|xz\rangle + 0.782|yz\rangle$ for YTiO$_3$. Hence, it is nearly identical with the ones we obtained from the LDA as having the lowest energy. For YTiO$_3$ our orbital is similar to the one obtained in Ref. [16] and for LaTiO$_3$ it is similar to the one obtained in Refs. [9,15]. Our accurate Wannier functions show why these orbitals (Fig. 1, left panels) have the lowest energy: The positive (blue) lobes have bonding $3z^2$ character on the nearest cations — those along [111] — and the negative (red) lobes have bonding $xy$ character on the next-nearest cations — those along [111] — whose oxygen surrounding is favorable for this type of bond, i.e., where $(Op)(Yxy)$ pdd hybridization is strong. The former type of AB covalency dominates in LaTiO$_3$, while the latter dominates in YTiO$_3$, where the shortest YO bond is merely 10% longer than the TiO bond. The difference seen (Fig. 1, right panels) between the orbital orders in the two compounds is therefore quantitative rather than qualitative; it merely reflects the extent to which the orbital has the bc plane as a mirror. The two different JT distortions of the oxygen square are reactions to, rather than the causes of the difference in the orbital orders. This difference is reflected in the hopping integrals between nearest neighbors: $t_x = t_z = 99$ (38) meV and $t_y = 105$ (48) meV for LaTiO$_3$ (YTiO$_3$). These hoppings are fairly isotropic and twice larger in LaTiO$_3$ than in YTiO$_3$. Moreover, the hoppings to the two excited orbitals are stronger in YTiO$_3$ than in LaTiO$_3$. All of this is consistent with LaTiO$_3$ being G-type anti- and YTiO$_3$ ferromagnetic at low temperature, and it warrants detailed future calculations of the spin-wave spectra.

In conclusion, we have extended the LDA + DMFT approach to the noncubic case using ab initio downfolding in order to obtain a low-energy Wannier Hamiltonian. Applying this method to the Mott transition in 3d$^1$ perovskites, we have explained the photoemission spectra and the values of the Mott gap without adjustable parameters, except a single value of $U$. The Mott transition is driven by correlation effects and GdFeO$_3$-type distortion through reduction, not only of bandwidth, but also of effective orbital degeneracy. Correlation effects and cation covalency suppress orbital fluctuations in the high-temperature paramagnetic insulating phase of LaTiO$_3$ and YTiO$_3$.

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References

[13] By 0%, 10%, 13%, and 21% of the average OA distance.
[14] By 0%, 3%, 4%, and 10% of the average AB distance.
[25] $\Sigma_{\text{min}(\nu_m)}(\omega) \neq 0$ in noncubic systems, also in the eigenrepresentation of the density matrix. In Fig. 2, a large $N_{\text{min}(\nu_m)}$ points to a large $\Sigma_{\text{min}(\nu_m)}$.
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